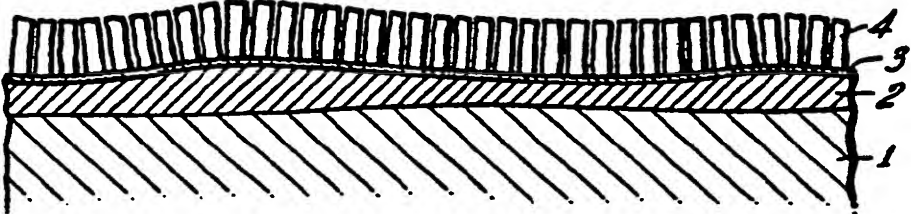


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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US93/10860 <b>(22) International Filing Date:</b> 10 November 1993 (10.11.93)  <b>(30) Priority Data:</b> 07/995,313                      22 December 1992 (22.12.92)      US  <b>(71) Applicant:</b> UNITED TECHNOLOGIES CORPORATION [US/US]; Patent Department - MS 132-13, One Financial Plaza, Hartford, CT 06101 (US).  <b>(72) Inventor:</b> GUPTA, Dinesh, K.; 29 Wildwood Circle, South Windsor, CT 06074 (US).  <b>(74) Agent:</b> SOHL, Charles, E.; Pratt & Whitney, Patent Department - MS 132-13, 400 Main Street, East Hartford, CT 06108 (US).		<b>(81) Designated States:</b> JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> COLUMNAR CERAMIC THERMAL BARRIER COATING WITH IMPROVED ADHERENCE  <b>(57) Abstract</b> <p>The coated article and a method for producing the coated article are described. The article is coated with an effective columnar grain ceramic thermal barrier coating. Between the substrate and columnar ceramic coating is an inner layer of a specific composition which provides for enhanced durability and resistance to spallation.</p> 		

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## Description

### Columnar Ceramic Thermal Barrier Coating With Improved Adherence

#### Technical Field

The present invention relates to the field of ceramic coated metal substrates. More particularly, the present invention is concerned with metal substrates having columnar grain ceramic thermal barrier coatings suitable for use at elevated temperatures.

#### Background Art

It is known in the aerospace field to provide enhanced temperature capabilities for metallic substrates through the provision of insulating coatings. Specifically, in the field of gas turbine engine technology, it is known to apply ceramic thermal barrier coatings to superalloy components such as blades, vanes and other hardware. Particularly where the hardware is internally cooled, the provision of thin ceramic coatings can provide significant reductions in temperature and thereby enhanced component life. Alternately, if desired, the engine can be operated at a hotter temperature so as to provide the same temperature in the substrate which would otherwise be encountered without the coating, and enhanced performance or fuel economy can be obtained.

A most successful type ceramic thermal barrier coatings is one which is called a columnar ceramic thermal barrier coatings. In this type of coating the ceramic coating comprises a multiplicity of thin columnar constituents, which is separated from each other by thin cracks. Each constituent is firmly bonded to the substrate at one end. The advantage provided by

the cracks is that the substrate expansion and contraction can be accommodated in the coating by simply allowing for a very limited expansion of the existing cracks. Thus, in a sense, by providing a controlled precracked coating enhanced durability results.

The general subject of columnar grain ceramic thermal barrier coatings is extensively described in U.S. Patent Nos. 4,321,310, 4,321,311, 4,401,697, 4,405,659, 4,405,660 and 4,414, 249, which are incorporated herein by reference.

According to those patents, the metallic substrate, typically a nickel base superalloy, is provided with a bond coat of the MCrAlY type where M is a metal chosen from the group consisting of iron, nickel and cobalt. This columnar ceramic thermal barrier coatings is supplied by vapor deposition under controlled conditions. An important feature of this type of coating is the existence of an alumina layer firmly bonded to the MCrAlY bond coat and simultaneously bonded to the fixed ends of the columnar ceramic segments.

These patents describe variations on this theme, including polishing the bond coat so as to provide enhanced smoothness and thereby an improved adherence and other variations for producing columnar grain ceramic thermal barrier coatings.

Two later patents, U.S. Patent Nos. 4,880,614 and 4,916,022 also deal with the subject of columnar ceramic thermal barrier coatings. U.S. Patent No. 4,880,614 suggests that improved durability can result by the provision of a high purity alumina interfacial layer between the bond coat and the ceramic coat. In particular, it is suggested that an aluminizing step be

performed on the bond coat prior to the application of the ceramic thermal barrier coatings layer. U.S. Patent No. 4,916,022 suggests that a compositional modification of the ceramic thermal barrier coatings layer can improve enhanced durability. Specifically, what is suggested is the addition of titania to that portion columnar ceramic thermal barrier coatings which is adjacent to the bond. These two patents are incorporated herein by reference.

The subject of MCrAlY coatings has received extensive development, and subsequent to the issuance of the six patents first referred to above, an improved MCrAlY coating composition was described in U.S. Patent No. 4,419,416 which was subsequently reissued as RE 321,121. This reissue patent is incorporated herein by reference. The teaching of this patent is that the performance of an MCrAlY material, when used alone for oxidation resistance, can be substantially improved by the addition of a combination of silicon and hafnium, specifically from 0.1 to 7% silicon and 0.1 to 2% hafnium in a conventional MCrAlY composition. A specific composition range described in this patent comprises 15-25% chromium, 10-20% aluminum, up to 30% cobalt, 0.1-2% yttrium, balance essentially nickel, along with the previously mentioned hafnium and silicon additions.

#### Brief Description of The Drawings

The figure shows a schematic of a coating according to the present invention.

## Disclosure of Invention

The present invention arises from the discovery that the substitution of an MCrAlY bond coat containing both hafnium and silicon into existing columnar grain ceramic thermal barrier coatings as taught in U.S. Patent Nos. 4,321,310, 4,401,697, 4,405,659, 4,405,660 and 4,414,249 can substantially enhance the long-term durability of this type of columnar grain ceramic thermal barrier coatings.

The invention includes a composite coating system which protects metallic articles from environmental damage especially under conditions of high temperature. The coating will generally be applied to a superalloy substrate. Table 1 lists examples of common superalloy materials to which the invention coating can be applied.

TABLE 1

	Cr	Co	Al	Ti	Mo	W	Ta	Cb	V	C	Fe	Ni
IN 100	10	15	5.5	4.7	3.0	-	-	-	1.0	.18	-	Bal
MAR M200	9	10	5.0	1.0	-	12.5	-	1.0	-	.15	-	Bal
MAR M509	24	Bal	-	.2	-	7	7.5	-	-	.6	1.0	10
WI 52	21	Bal	-	-	-	11	-	2	-	.45	2	-

The article to be protected is supplied with a uniform adherent MCrAlY+Hf+Si layer. On this MCrAlY+Hf+Si layer, there is applied a columnar ceramic coating.

The metallic layer is comprised of a MCrAlY+Hf+Si alloy which has a broad composition of 5 to 40% chromium, 8 to 35% aluminum, 1 to 2.0% yttrium, .1-7% silica, .1-2.0% hafnium and the balance ("M") selected from the group consisting of iron, cobalt, nickel and mixtures thereof.

It is preferred that this MCrAlY+Hf+Si layer be applied by vapor deposition. Such a deposition process in combination with (optional but preferred) peening and heat treating (4 hours at 1975°F) provides a dense adherent layer of relatively uniform thickness which is basically free from defects. A thickness of 1-10 mils is suitable.

Other deposition process may be employed for producing the MCrAlY+Hf+Si layer including sputtering and plasma spraying, possibly with associated post coating treatments, so long as they produce an adherent uniform thickness high integrity coating of the desired composition.

The alumina layer on the MCrAlY+Hf+Si layer is produced by oxidation of the MCrAlY+Hf+Si layer. Oxidation may be in air or even commercially pure hydrogen. This oxide layer is relatively thin (0.01-0.1 mil), uniform and adherent. Adherence of the oxide layer is greatly improved in MCrAlY+Hf+Si alloys compared to that of similar alloys which do not contain the combination of yttrium, hafnium and silicon.

The final component of the thermal barrier coating is a columnar grained ceramic surface coating which is tightly bonded to the alumina layer. The columnar grains are oriented substantially perpendicular to the surface of the substrate with free surfaces between the individual columns extending down to the aluminum oxide layer.

The columnar nature of the surface layer circumvents the difference in the coefficients of thermal expansion between the substrate and the coating which is believed responsible for failure in prior art ceramic thermal barrier coatings. Upon heating, the substrate expands at a greater rate than the ceramic surface coating and the columnar boundaries between the individual ceramic columns open to accommodate mismatch strains. This limits the stress at the interface between the substrate and the columnar ceramic to a level below that which will produce a fracture of a columnar surface layer. The columns have dimensions on the order of 0.1 mil in cross section.

The columnar surface layer may be any of many ceramic compositions. Most of the experimental work to date has been performed with a ceramic composed of zirconium oxide stabilized by the addition of either 20 or 35% yttria to ensure a cubic structure at all temperatures of interest.

The columnar grain ceramic surface layer reduces the temperature of the underlying substrate and coating layers. Because of the nature of many ceramics and the existence of the open boundaries between the columns, the ceramic surface layer is relatively transparent to oxygen and does not play a major role in reducing the oxidation of the underlying layers except to the extent that the reduction in the temperature of the underlying layers reduces the rate of oxidation. Preliminary indications are that a 5 mil thick  $ZrO_2$  base coating can reduce substrate temperatures by from 50° to 200°F under conditions typical of those found in current gas turbine engines with cooled blades.

The Figure shows a cross sectional line drawing of a coating according to the present invention. The

substrate material 1 is coated with an MCrAlY+Hf+Si layer 2. On this layer 2, there is formed an adherent alumina layer 3. Finally, a columnar ceramic layer 4 adheres to the alumina layer 3.

5

#### Best Mode For Carrying Out The Invention

Having described the structure of the coated article, we will now describe a preferred method of producing this coating on gas turbine components such as blades and vanes.

10

The initial step is the preparation of the surface to be coated. The surface must be clean of all dirt, grease, oxides and the like.

The cleaning method I have used is vapor honing in which an aqueous abrasive slurry is propelled against the surface to be cleaned with sufficient force to remove all extraneous material from the surface. Following this step, the surface is preferably vapor degreased. While this is a satisfactory cleaning process, numerous alternative processes are possible.

15

20

Next, the MCrAlY+Hf+Si layer is applied. It is preferred that this MCrAlY+Hf+Si layer be applied by vapor deposition. The deposition process is performed by holding the surface to be coated over a pool of molten MCrAlY+Hf+Si material in a vacuum chamber. The heat source used to keep the MCrAlY+Hf+Si molten is usually an electron beam.

25

30

The surface to be coated is preferably maintained at a temperature of about 1600°-1800°F during the MCrAlY+Hf+Si deposition process.

It is preferred that the MCrAlY+Hf+Si layer have a thickness of about 1 to about 10 mils. MCrAlY+Hf+Si thicknesses below about 1 mil do not provide adequate protection to the surface and thicknesses in excess of

about 10 mils are prone to rippling during repeated thermal cycling.

5 In conventional MCrAlY+Hf+Si practice, the coatings are dry glass bead peened to density any voids and to improve the coating structure. Such peening is preferred, but has not been found essential.

10 The coating is then preferably heat treated at 1975°F in hydrogen, however neither the time nor temperature is particularly critical. I have used a 4-hour treatment to improve the adherence of the coating to the substrate.

15 In the particular preferred processing sequence, this hydrogen heat treatment also serves to develop the desired alumina layer. This oxidation occurs as a result of oxygen impurities in the hydrogen. I have also employed a separate oxidation step in air in the temperature range of about 500°-2000°F and the results appear to be similar.

20 It also appears possible to develop the alumina layer after the deposit of the columnar grained ceramic layer. This is especially likely in the case of zirconia based ceramics which are quite transparent to oxygen. However, formation of the alumina layer prior to the columnar grained ceramic layer deposition is preferred.

25 Following the application of the MCrAlY+Hf+Si layer and the development of the oxide layer, the columnar grained ceramic surface layer is applied by a vapor deposition process.

30 The ceramic to be deposited is melted and maintained as a molten pool or evaporation source. We have used 10-20 mesh ceramic powder as a starting material although other starting forms are also satisfactory. The substrate to be coated is positioned

over the evaporation source and is manipulated to produce a uniform coating thickness and to enhance the production of a columnar structure. The ceramic coating thickness may range from about 1 to about 50 mils.

5           During the ceramic coating cycle, it has been found desirable to maintain the substrate at a relatively low temperature, e.g., 1000°-1500°F to provide a relatively coarse columnar structure and a relatively stoichiometric coating composition.

10           In cyclic testing at 2075°F where a cycle consisted of 4 minutes in the flame and 2 minutes in a cooling air jet, a columnar grain thermal barrier coating on a NiCoCrAlY bond coat (without Si or Hf) lasted about 100 hours (a range of 85-136 hours). A  
15           similar sample on a NiCoCrAlY+Hf+Si bond coat according to the invention lasted about 300 hours (220-500 hour range).

20           Although this invention has been shown and described with respect to detailed embodiments thereof, it will be understood by those skilled in the art that various changes in form and detail thereof may be made without departing from the spirit and scope of the claimed invention.

## CLAIMS

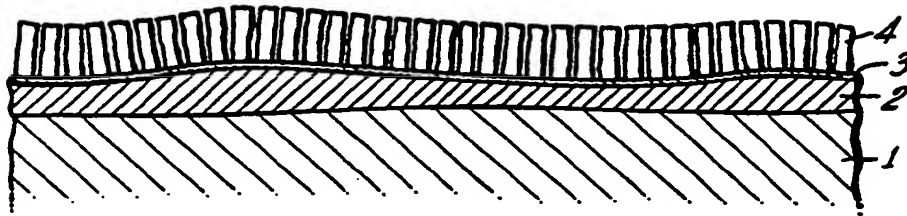
I claim:

1. A superalloy article having an adherent durable ceramic thermal barrier coating including:
  - a. a superalloy substrate,
  - b. an adherent dense coating consisting  
5 essentially of MCrAlY+Hf+Si on the substrate where M is selected from the group consisting of iron, nickel, cobalt and mixtures of nickel and cobalt,
  - c. an alumina layer on the MCrAlY+Hf+Si coating  
10 surface,
  - d. an adherent columnar layer, consisting essentially of ceramic, on the alumina layer.
2. A coated article as in claim 1 in which the thickness of the MCrAlY+Hf+Si is from about 1 to about 10 mils.
3. A coated article as in claim 1 in which the columnar ceramic coating has a thickness of from about 1 to about 50 mils.

4. A superalloy article having an adherent durable ceramic thermal barrier coating including:

- a. a superalloy substrate,
- b. an adherent dense coating consisting essentially of MCrAlY+Hf+Si substrate, where M is selected from the group consisting of iron, nickel, cobalt and mixtures of nickel and cobalt,
- c. an alumina layer on the MCrAlY+Hf+Si coating surface, having a thickness of from about 0.01 to about 0.1 mils,
- d. an adherent columnar layer, consisting essentially of ceramic, on the alumina layer.

5. An article as in claim 1 or 4 in which the columnar ceramic consists essentially of stabilized zirconia.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/10860

A. CLASSIFICATION F SUBJECT MATTER  
IPC 5 C23C28/00 F01D5/28

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,92 05298 (UNITED TECHNOLOGIES CORPORATION) 2 April 1992 see claims 1-5 -----	1-5

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9205298	02-04-92	AU-A- 8728191	15-04-92